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**TOWARDS A PATENT FOR A NEW WASTEWATER
TREATMENT PROCESS: CHEMICALLY ENHANCED
PRIMARY WASTEWATER TREATMENT AND THE USE
OF CHITOSAN IN CHEMICALLY ENHANCED
PRIMARY WASTEWATER TREATMENT**

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**by Susan Murcott
May, 1991**

ABSTRACT

This paper describes two inventions. The first invention is "chemically enhanced primary wastewater treatment" which is a unique application of known processes. The defining characteristic of this wastewater treatment method is the maximization of the efficiency of the first stage in the wastewater treatment regime. Chemically enhanced primary wastewater treatment is distinguished from other methods of chemical wastewater treatment by small dosages of a metal salt(s) (< 50 mg/l), small dosages of a polyelectrolytic polymer(s) (< 1.0 mg/l), high overflow rates, and minimal follow-on biological treatment approximately 50 percent reduced in size compared to standard wastewater treatment schemes. This invention has been developed through the joint efforts of Donald R.F. Harleman, Shawn Morrissey, and Susan Murcott.

The second invention is the application of chitosan in chemically enhanced primary wastewater treatment. This second invention is the joint work of Donald R.F. Harleman and Susan Murcott.

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PART I -- CHEMICALLY ENHANCED PRIMARY WASTEWATER TREATMENT

**1.0. INTRODUCTION AND BRIEF DESCRIPTION OF CHEMICALLY ENHANCED
PRIMARY WASTEWATER TREATMENT**

Article I, Section 8 of the United States Constitution establishes the basis for patents to "promote the progress of the useful arts by securing for limited times to inventors the exclusive right to their discoveries." There are five classes of patentable inventions: 1) a process; 2) a machine; 3) a manufacture; 4) a composition of matter or a material; and 5) any new and useful improvement.

This paper explores the idea that chemically enhanced primary wastewater treatment, and the use of chitosan in chemically enhanced wastewater treatment, are patentable inventions. Chemically enhanced primary wastewater treatment comes under the class of a "process" and a "new and useful improvement." Process has been defined as "a process, art or method ... usually embracing a series of steps for accomplishing or producing a certain result."¹ Process can also mean "a new use of a known process."²

The invention called "chemically enhanced primary wastewater treatment" is a new and unique application of known processes. The defining characteristic of this wastewater treatment method is the maximization the efficiency of the first stage in the wastewater treatment regime. Chemically enhanced primary wastewater treatment is characterized by small dosages of a metal salt(s) (< 50 mg/l), small dosages of a polyelectrolytic polymer(s) (< 1.0 mg/l), high overflow rates, and minimal follow-on biological treatment approximately 50% reduced in size. Each of these individual characteristics has been known previously, but this combination of elements has not been conceived of in wastewater treatment design (and in fact has been strenuously resisted by the design professionals, environmentalists and Environmental Protection Agency regulators).

2.0 BACKGROUND

2.1 TYPES OF WASTEWATER TREATMENT SYSTEMS

Wastewater contains a variety of kinds of contaminants: total suspended solids (TSS) and biochemical oxygen demand (BOD), the so-called "conventional pollutants;" nutrients (phosphorus and nitrogen); toxics (heavy metals or organic pollutants); and pathogens, (bacteria and viruses). Wastewater treatment can use one of three means to purify the polluted water: physical means, biological means, or chemical means.

Primary treatment uses physical means, i.e. gravity, to allow conventional pollutants to settle out in large settling tanks. A well-run primary treatment plant typically removes 60% of TSS and 35% of BOD.

Biological treatment is often called "secondary treatment" as it usually follows after primary treatment. Biological treatment makes use of specific kinds of bacteria added into an additional series of tanks downstream of the primary tanks. The bacteria's job is to munch away at smaller particles of waste, thereby achieving approximately 85% removal of TSS and BOD. In the United States today, the typical treatment system is a combination of primary and (biological) secondary.

Chemical treatment takes two forms. Chemically enhanced primary adds a quantity of chemicals to primary tanks to achieve approximately 80% removal of TSS and 57% removal of BOD.

"Chemical secondary" involves the use of somewhat larger quantities of chemicals to achieve over 85% removal of TSS and 85% removal of BOD.

Tertiary treatment makes use of either chemical and/or biological methods. Typically, tertiary treatment focuses on the removal of nitrogen and/or phosphorus, the nutrients responsible for eutrophication of lakes and rivers.

2.2 HISTORICAL BASIS FOR WASTEWATER TREATMENT STAGES

The sequence of stages found in wastewater treatment plants today came about for historical reasons. Although the collection of storm water and drainage dates back to ancient times, the collection of wastewater can be traced to the early 1800s. The impetus for innovation in this field was the emerging understanding of the relationship between pollution and disease. The development of the germ theory in the latter half of the 19th century by Koch and Pasteur marked the beginning of modern sanitation.³ During the 19th century in England, France, the United States, primary wastewater treatment became the state-of-the-art technology for handling urban sewage and protecting public health.

In the early to mid-20th century, primary treatment alone did not always provide sufficient removal of conventional pollutants, thus a second stage of treatment, typically using a biological treatment method, was added to the primary stage. More recently, as the eutrophication of lakes and other surface waters has become widely recognized as a serious problem, a tertiary stage has been added.

In the last two decades, the bureaucratic tendencies of the environmental regulators, the technical naivete of the environmentalists, plus the conservatism and mercantilism of wastewater design engineers, has combined to stifle innovation in the field of wastewater treatment technology. Bigger is seen as better, more treatment stages are preferred to fewer. The Clean Water Act of 1972, for all it has accomplished in terms of improving water quality and increasing the level of wastewater treatment, has frozen innovation in wastewater treatment design in the United States. (See Appendix A -- Testimony to the Water Resources Subcommittee of the Committee on Public Works, House of Representatives, March 24, 1990, by S. Murcott). By establishing "technology-based requirements," specifically by mandating nation-wide secondary treatment, the Clean Water Act has greatly favored a treatment regime of primary treatment followed, typically, by the activated sludge biological treatment process, and then possibly by a tertiary stage. 76% of treatment plants in the United States have this biological treatment stage, of which 22% follow this up with a tertiary treatment stage (Figure 1: *Overview of Wastewater Treatment in the United States*).⁴

While the performance of inadequate wastewater treatment systems can be improved by adding an additional stage in the treatment train, design engineers, even when starting from scratch, as for example in the clean up of Boston Harbor, have assumed the use of conventional primary followed by the activated sludge biological secondary treatment process. More recent experience however has shown that the same results can be achieved both with fewer and with smaller stages. The guiding principle behind this improvement is the idea of maximizing the efficiency of the primary stage.

Until now, design engineers have paid little heed to the notion of maximizing primary treatment efficiency, to the point where supposed state-of-the-art plants show sub-standard primary treatment removal rates (Figure 2: Orange County South Water Reclamation Facility, Orlando, Florida) because it is assumed that the second and third treatment stage will accomplish the desired end. Alternatively, engineers have eliminated primary treatment altogether (Figure 3: Pompano Beach Wastewater Treatment Facility, Pompano Beach, Florida, and Figure 4: Water Conservancy Wastewater Treatment Facility, Orlando, Florida) on the assumption that primary treatment provides only a small degree of treatment.

2.3 USE OF CHEMICALS IN WASTEWATER TREATMENT

The first attempts at chemical sewage treatment were made in Paris in 1740. In the succeeding 100 years, chemical treatment practices became established in England, where, by 1875, more than 400 patents were issued. Few of these, however, were found to be of practical value.⁵ The first plant to use chemical wastewater treatment in the United States was built in 1886, and in the next 10 years, several other plants followed suit. Nevertheless, the popularity of chemical wastewater treatment was short-lived -- it never met with as much favor as it had in England -- and the development of biological processes in the early 1920s led to the abandonment of most of these early efforts.

A renewed interest in chemical treatment was sparked by a 1929 article describing the benefits of using ferric chloride in the primary settling process.⁶ From then until the present, treatment plants have sometimes used chemical addition in the primary, secondary, and/or tertiary stages. This now out-dated chemical treatment method involved the addition of relatively large quantities (100 - 250 mg/l) of ferric chloride, lime, alum, or other metal salt(s). As sludge disposal became an increasing burden, this process (which has come to be thought of as the only form of chemical wastewater treatment), lost favor, insofar as large quantities of chemicals generate large quantities of sludge. Also, the high cost of chemicals contributed to its bad reputation.

In the late 1970s and early 1980s, synthetic polymers have begun to be used in conjunction with metal salts in wastewater treatment allowing the reduction in the amount of metal salt needed.*

Nevertheless, until now, this development in chemical technology has not been accompanied by a simultaneous rethinking of wastewater treatment plant design.

At present, chemical wastewater treatment** is used in four specific applications. Table 1 gives these applications and indicate all of the plants in the United States that use chemical addition in the primary stage and some of the notable examples in

* It should be pointed out the term "chemically enhanced wastewater treatment" does not refer to the use of chlorine directly before discharging a plant's final effluent, nor does it cover the use of polymers and other sludge thickeners in sludge handling processes. Chemically enhanced wastewater treatment is a term coined by Donald R.F. Harleman to refer to the use of metal salts and/or polymers in the liquid treatment process prior to final disinfection.

** The term "chemical wastewater treatment" will be used to designate the "old" chemical wastewater treatment methods. The

term "chemically enhanced treatment" will refer to the "new" invention described in this paper. Canada and Europe. This list is presented in order to show what exists to date as far as chemical addition in wastewater treatment applications is concerned. We can then use this as a point of departure for describing and contrasting the chemically enhanced primary wastewater treatment process, which is a "new use of a known process."

TABLE 1
UNITED STATES WASTEWATER TREATMENT PLANTS
USING CHEMICAL ADDITION IN THE PRIMARY STAGE

I. PLANTS USING CHEMICAL ADDITION FOR CHEMICAL PRIMARY TREATMENT ONLY

San Diego, CA
Windsor, Ontario

Sarnia, Ontario
Longueil, Ontario

II. PLANTS USING CHEMICAL ADDITION FOR CHEMICAL PRIMARY TREATMENT + A FOLLOW-ON TREATMENT STAGE(S)

Los Angeles (Hyperion), CA
Orange County, CA
Sacramento, CA
Gainesville, GA.
Medway, MA
Cortland, NY
Erie, PA

Los Angeles County, CA
San Clemente, CA
Pensacola, FL
Leominster, MA
Fort Meade, MD
North Tonawanda, NY
Alexandria, VA

III. PLANTS USING CHEMICAL ADDITION FOR PHOSPHORUS REMOVAL

Hartford, MI
Escanaba, MI
Mason, MI
Flint, MI
Lima, OH
Oak Creek, WI
Cleveland (Easterly), OH
Berlin, Germany

Marine City, MI
Charlotte, MI
Romeo, MI
Rocky River, OH
Grafton, WI
Saukville, WI
Oslo, Norway

IV. SECONDARY OR TERTIARY PLANTS WHICH HAVE FAILED AND/OR BEEN SHUT DOWN AND WHICH HAVE BEEN RETROFITTED WITH CHEMICAL TREATMENT AS A TEMPORARY OR PERMANENT MEASURE

West Fitchburg, MA
New York, NY

Niagara Falls, NY
Cleveland (Westerly), OH

V. PLANTS USING CHEMICAL ADDITION FOR CHEMICAL SECONDARY TREATMENT

Tacoma, WA

Oslo, Norway

Table 1 lists the various applications of chemical wastewater treatment to date.

Chemical treatment is used to achieve what has often been called "advanced primary" treatment, possibly as a single stage, stand-alone process, as in the case of San Diego, California or several facilities in Ontario (Category I), or as the first stage in a multi-stage process (Category II). It is used at plants in the Great Lake States (Category III) to meet a phosphorus discharge standard, the addition of metal salts plus a synthetic polymer having been found to be a simple and effective way to remove high levels of phosphorus.

Chemical addition is also used to maintain a good degree of removal of conventional pollutants when a secondary or tertiary treatment plant has been shut down and/or failed (Category IV). The plants in Niagara Falls, N.Y.; Cleveland, Ohio; and New York, N.Y.; are the notable examples in this category.

Chemical addition can be used to achieve chemical secondary treatment (Category V). Unfortunately, to date this has only been accomplished by returning to the so-called "old" method of chemical treatment, that of using large quantities of metal salts, albeit, supplemented with certain polymers.

The information of Table 1 shows that chemical treatment in the primary stage is used in only 30 plants in the United States, (out of a total of over 16,000 municipal wastewater treatment plants⁷). The EPA has not evaluated the application of polymer chemistry in primary wastewater treatment. The EPA keeps almost no statistics on chemical treatment and the information provided in Table I has been painstakingly culled from indirect EPA sources.

To sum up this historical review of chemical addition in wastewater applications, experience to date with chemical treatment in primary wastewater applications has generally involved large doses of alum or lime and produced massive quantities of sludge. The single stage alum/lime treatment process has been found to be uneconomical compared to the conventional two-stage primary/secondary treatment regime and has been generally discounted.

3.0 DESCRIPTION OF CHEMICALLY ENHANCED PRIMARY WASTEWATER TREATMENT

Figure 5 compares conventional primary and activated sludge biological secondary wastewater treatment with chemically enhanced treatment in the "new" applications which are the subject of this patent. We see that chemically enhanced treatment can perform comparable to or better than biological treatment in terms of removal of conventional pollutants. Chemically-enhanced treatment will remove 25% more total suspended solids, and 39% more biochemical oxygen demand than conventional primary treatment. In addition, chemically enhanced treatment removes a

much higher percentage of phosphorus, one of the principal nutrients causing eutrophication and nuisance algal blooms. It will take out 80% or more of phosphorus, as opposed to only 15% with biological secondary treatment. Chemically-enhanced primary treatment will fall slightly short of the full secondary treatment requirement in terms of TSS and BOD removal. This additional removal can be accomplished with a minimal follow-on biological treatment step.

There are 3 defining characteristics of the "new" method of chemically enhanced primary wastewater treatment that give the results shown in Figure 5.

- 1) Small dosages of a metal salt(s) (< 50 mg/l) and a polyelectrolytic polymer(s) (< 1.0 mg/l)
- 2) High overflow rates;
- 3) Minimal follow-on biological treatment approximately 50% reduced in size.

An efficient sewage treatment plant is one that can run using minimal chemical dosages and yet maintain a high overflow rate while sustaining a high pollutant removal rate. If any additional treatment is required, an efficient process seeks to maximize the first stage of treatment in order to minimize the size and complexity of any follow-on stage. While this seems like nothing more than common sense, it has not been common practice. The invention described in this paper translates these common sense ideas into procedures.

3.1 SMALL CHEMICAL DOSAGES

Experience with chemically enhanced primary wastewater treatment using small amounts of environmentally-safe chemicals and an anionic polyelectrolytic polymer to promote clumping together of smaller particles into larger particles (called "coagulation" and "flocculation"), has as its basis work that has taken place in the past ten years in southern California and Scandinavia. Recent advances have mainly been pioneered at Ralph M. Parsons Laboratory at the Massachusetts Institute of Technology. The new procedures that allow the use of much smaller quantities of chemical have come about as a result of developments in polymer chemistry. Thus where 100 - 250 mg/l of metal salts have once been used, these new methods allow the use of less than 50 mg/l.

3.2 HIGH OVERFLOW RATES

Chemically enhanced treatment is a more efficient process in that a higher overflow rate can be sustained. The overflow rate is the standard measure of flow through the plant, specifically it is the number of gallons per day per area of tank surface (typically expressed as "gallons per day per foot squared" or "gpd/ft²"). A chemically enhanced primary plant can consistently be operated at two times the efficiency of a conventional primary treatment plant.

The success of present-day chemical primary treatment must be measured against the expected removal efficiencies and overflow rates of conventional primary treatment plants. As shown in Figure 6, the design condition for annual average overflows for conventional primary treatment is about 800 gpd/ft² and results in removal rates of 60 percent for TSS and 35 percent for BOD. Conventional primary treatment efficiency decreases rapidly as flow through the plant increases. For example, at an overflow rate of 2,400 gpd/ft², which is three times the average, the removal rates drop to about 37 percent for TSS and 17 percent for BOD.

The effectiveness of chemically enhanced primary treatment in sustaining high removal efficiencies at high overflow rates is shown in Figure 7. The results illustrated in this figure are from full plant tests carried out more than ten years ago in Sarnia, Ontario at a conventional primary plant.⁸ Very little decrease in treatment efficiency is observed at overflow rates as high as 2750 gpd/ft². Annual average results for 1989 at the same primary plant are shown in Figure 8. It is significant that with the addition of only 14 mg/l of ferric chloride and 0.3 mg/l polymer, the TSS and BOD removals averaged 84% and 60% respectively.

3.3 CHEMICALLY ENHANCED PRIMARY TREATMENT PLUS BIOFILTERS

The effect of the chemical addition in combination with high overflow rates means that significantly larger amounts of BOD are removed in the primary stage of treatment. Whereas conventional primary treatment removes only 30% of BOD, chemically enhanced primary treatment consistently removes 57% BOD. This optimization of the primary stage effects any follow-on treatment. The result is a 50% reduction in size of any follow-on treatment, whether activated sludge or a biofilter technology. However, because the activated sludge biological secondary treatment process is not as efficient as biofilters in dealing with low BOD influents, the advances described here in chemical technology suggest a new role for high rate aerated filters and other attached growth processes. Biofilters, simpler and hitherto less well-regarded technologies, may become the major biological component in a system that takes advantage of all the above-mentioned components.

4.0 PROCEDURE FOR CHEMICALLY ENHANCED PRIMARY TREATMENT

Figure 9 is a generalized process diagram of a retrofitted primary treatment facility indicating the range of chemical concentration and points of addition. Figure 10 is a process diagram of a primary facility specifically designed to optimize the efficiency of chemical addition. The schematics are simply presented in this section, but not described in any depth because the more detailed procedural description is given in Part II (see Section 8.1). The procedures to be followed whether for metal salt addition or chitosan addition are identical.

As we will see in the discussion of chitosan in Part II, metal salts perform more or less comparably with chitosan, either acting in the capacity of what is called the "primary coagulant." The anionic polymer functions in the same role with either the metal salt or the chitosan. The anionic polymer is called the "coagulant aid." The chief difference between the use of the metal salt or the use chitosan is that smaller concentrations of chitosan are used, i.e. about half as much chitosan is needed.

5.0 DEMAND FOR THIS INVENTION

Figure 1 showed that 76% of wastewater treatment plants in the U.S. have secondary treatment, and of those, 22% also have tertiary treatment. It also showed that 12% of the wastewater treatment plants have less than secondary treatment. These plants are required by law to come into compliance with Clean Water Act's secondary treatment requirement. A relatively new twist to this regulatory requirement is EPA's recent de-emphasis on technology-based requirements and emphasis on simply meeting the standard by whatever means. This is meant to provide the wastewater municipalities and designer engineers with a modicum of flexibility and to get the EPA out of the wastewater technology business.

While 12% may seem a relatively small number of plants, the EPA estimates that the upgrade of these facilities will cost a minimum of \$24 billion.⁹ The \$24 billion figure represents only a fraction of what needed to upgrade the U.S. sewage treatment infrastructure. For example, the Boston Harbor cleanup is estimated to cost \$6.1 billion dollars (in 1999 dollars), but only one-half of that sum will go specifically towards meeting the secondary treatment requirement. The point is, there is a tremendous need for cost-effective technological innovation in this field.

Beyond the United States and other first world nations, Eastern Europe, the USSR, and the 3rd World have massive wastewater treatment problems. Sanitation issues are very much in the news right now with the Kurdish refugee problem and the cholera epidemic in Peru. Cost-effective innovations are of vital concern not only in this country but around the world.

PART II-- CHITOSAN

6.0 THE NATURAL POLYMER CHITIN AND THE DERIVED PRODUCT CHITOSAN

Chitosan is a natural, non-toxic, biodegradable, high molecular weight, cationic polymer. It is manufactured from chitin, the second most abundant natural polymer after cellulose. Like cellulose, chitin is a polysaccharide, a compound formed of many identical simple sugar molecules. Again like cellulose it is a B (1-4) - linked glycan, but is composed of 2-acetamide-2-deoxy-D-glucose (N-acetylglucosamine) (Figure 11). Chitosan is a linear polyamine whose amino groups are readily available for chemical reaction and salt formation with acids. It has a high charge density of one charge per glucosamine unit. The positive charge of chitosan interacts strongly with the negative charges of many materials making it an excellent flocculent.

The most available source of chitin is the shells of crustaceans. Natural chitin is bound by protein and calcium carbonate which can be removed to greater or lesser degrees by different purification techniques. Typically, the extraction process begins with grinding and removal of proteins enzymatically or with a dilute sodium hydroxide (caustic soda) solution, followed by removal of mineral components with dilute hydrochloric acid. Removal of acetyl groups at an elevated temperature (130 - 150 C) readily forms chitosan, the simplest derivative of chitin.

There are over 200 current or potential applications of chitin and chitosan in industry, medicine, biotechnology, food processing, agriculture, and environmental protection.¹⁰ This paper will describe one application, the use of chitosan in municipal wastewater treatment. Its application in wastewater treatment has been mainly as a flocculent for recovering proteinaceous material. W.A. Bough of the Department of Food Science, University of Georgia Experiment Station, has investigated the efficacy of chitosan in the reduction of suspended solids in vegetable canning waste effluents (Bough, 1975), poultry processing wastes (Bough, 1975), egg breaking wastes, meat processing wastes, and fish processing wastes. (Bough, 1976). R.A. Johnson of the University of Alaska, Fairbanks, has compared the efficacy of chitosan in conjunction with ferric sulfate in treating seafood processing wastes. (Johnson, 1985). The Association of Animal Feed Control Officials, Inc. (AAFCO) describes chitosan as "a precipitation agent of proteinaceous material for food processing plants." (Sandford, 1989).

Chitosan, however, has not been employed in municipal wastewater treatment. The invention described below is for the specific application of chitosan in municipal wastewater treatment.

7.0 UNITED STATES CHITOSAN PATENTS

The manufacture of chitosan from chitin has been the subject of various patents.¹¹ George Rizby's 1938 patent describes a number of important processes for producing substantially undegraded deacetylated chitosan.¹² O.P. Peniston and E.L. Johnson hold some 8 chitosan patents.^{13,14,15,16,17,18,19,20} The first Peniston-Johnson patent (1970) made some claim to a new method of manufacturing chitosan -- presenting a method for manufacturing partially deaminated and partially deacetylated chitin for use in increasing the viscosity of liquids -- however, the major thrust of that patent was to give a range of applications for chitosan manufactured essentially by Rizby's methods.¹³ The 1970 Peniston/Johnson patent provided a method to treat an aqueous medium to remove an impurity by adding dissolved chitosan, forming an agglomerate of the impurity and the chitosan, separating the agglomerate from the aqueous medium by gravity settling or filtration, and discarding the agglomerate. The impurity is defined as:

1. a tannin;
2. a polyphenolic material;
3. a suspended solid;
4. an alkaline earth metal (calcium, magnesium, strontium, barium).

That patent is also a method of treating an aqueous medium using chitosan and a coagulant from the group consisting of an aluminum salt and a ferric salt.

Subsequent Peniston/Johnson patents have focuses almost exclusively on new methods of manufacturing chitosan. None of these patents have addressed themselves to the subject of maximizing the efficiency of municipal wastewater treatment processes through the use of chitosan.

The invention described below is therefore a further development and application of the inventions of Rizby and Peniston/Johnson.

8.0 DESCRIPTION OF THE USE OF CHITOSAN IN CHEMICALLY ENHANCED PRIMARY WASTEWATER TREATMENT

The Clean Water Act of 1972, and the Secondary Treatment Information Regulation established standards for TSS and BOD removal in municipal wastewater treatment plants (known by the acronym POTWs, "publically owned treatment works"). The standard requires that the POTWs 30-day average not exceed 30 mg/l TSS and 30 mg/l BOD, and also that they achieve 85% removal of TSS and BOD. In addition, municipalities have the option of substituting COD (carbonaceous oxygen demand) for BOD.

Various technologies have been employed to achieve this standard, although, as mentioned earlier, the dominant technology has been the activated sludge secondary treatment technology. Chitosan has never (to the author's knowledge), been used in municipal wastewater treatment applications to achieve TSS and BOD and/or COD removal. The Peniston/Johnson patent does describe the use of chitosan to remove suspended solids from an aqueous medium, and in this sense, the removal of TSS from municipal wastewater may fall within the range of their invention(although the patent is now expired). However, Peniston/Johnson do not describe a method to utilize chitosan for the removal of BOD or COD from wastewater. The removal of BOD or COD using chitosan is the subject of this [potential] patent. The use of chitosan to remove gross amounts of organic matter, as measured by tests such as the total organic carbon (TOC) test and the total oxygen demand (TOD) test also come under the rubric of this invention.

8.1 PROCESS FOR USING CHITOSAN TO REMOVE BOD, COD, TOC, AND/OR TOD FROM MUNICIPAL WASTEWATER

Laboratory Scale: Whether in the design of a new wastewater treatment facility or in a retrofit of an existing facility, laboratory scale jar testing is carried out as the first step in evaluating the efficacy of the chemical treatment process. Given the wide variation in municipal wastewaters: a function of the proportion of domestic to commercial to industrial sewage, of the type of industries present, of temperature and precipitation patterns, and of a variety of other factors, the purpose of jar testing is to determine the optimal dosage, mixing speed, and timing of chemical addition. More specifically, jar tests are a means to observe flocculation and settling intervals and to determine the optimal combination of the coagulant (chitosan) with the coagulant aid (the anionic polymer).

The procedure consists of adding varying concentrations of chitosan and an anionic polymer to the five of the six samples, mixing them simultaneously, allowing them to settle and observing the results. A control jar, the sixth jar, representing the chemically untreated sample, is run as a part of each series. All samples in the series should be handled as nearly alike as possible. Although the jar tests, as batch tests, do not exactly mirror the continuous flow conditions of a full scale plant, it is nonetheless important to simulate plant conditions as closely as possible in terms of the timing of chemical addition and the mixing speeds.

A general procedure, which should be modified to fit the conditions of the specific plant, is as follows:

Using a Phillips-Bird Gang Stirrer,

1. Place 800 ml wastewater sample in each of the six 1000 ml beakers.
2. Stir at 100 rpm.
3. Add 5 - 25 mg/l chitosan, stir at 100 rpm for 2.5 minutes.
4. Add < 1.0 mg/l anionic polymer (which has been prepared in accordance with manufacturer's specifications), stir at 100 rpm for 30 seconds.
5. Slow to 20 rpm. Stir for 1 minute.
6. Stop. Allow solution to settle for 5 to 10 minutes. Observe flocculation and settling rate.
7. Using a 100 ml syringe, decant 150 ml sample from 200 ml below the surface for analysis.

Full Plant Scale (in retrofitted primary wastewater treatment facilities, i.e. those not specifically designed for chemical addition)

Once optimal chemical concentration and the appropriate anionic polymer has been determined through jar testing, full scale testing and operation may proceed. Existing primary treatment plants may be retrofitted to allow chemical addition. Figure 12 shows the range of possible dosages and the points of chemical addition when using chitosan and an anionic polymer in a retrofitted facility. The chitosan is added to the influent flume prior to the grit chamber. The concentration is within the range of 5 to 25 mg/l. The anionic polymer is added after the grit chamber and before the primary clarifier in a maximum concentration of 1.0 mg/l.

Full Plant Scale (in facilities designed for chemical addition):

Obviously a facility designed for chemical addition can provide the optimal conditions for maximizing the efficiency of chitosan and anionic polymer to remove organic materials. Such a facility differs from a conventional primary treatment facility chiefly in the inclusion of both a rapid mix basin and a series of flocculation tanks after the grit chamber. For such a plant, the chemical addition dosage remains the same as discussed above, but the application points differ. These application points are indicated in Figure 13.

9.0 DEMAND FOR THIS INVENTION

The use of chitosan in wastewater treatment has a particular appeal because it involves recycling a waste product which is at the same time a naturally-occurring, biodegradable chemical in the environment. Shrimp and crab are especially good sources of chitin. D. Knorr estimates that the United States produces 45,000 metric tons of shrimp and crab processing wastes annually.²¹ Additional sources of chitin are the shells of lobster and various fungi.

In the United States today, some 1,906 wastewater treatment plants receive less than secondary treatment.²² This represents over 5000 million gallons per day of only partially treated wastewater.²³ To treat even half of that wastewater, 35,000 metric tons of chitosan per year (assuming a concentration of 10 mg/l), or roughly three-quarters of the shrimp/crab chitin solid wastestream, would be recycled into this valuable reuse. In addition, were chitosan manufacturing facilities set up in the neighborhood of fish processing plants, underemployed and unemployed fishermen would be given an opportunity to continue their work with products from the sea. This could be a valuable asset for many coastal communities such as New Bedford, Massachusetts, Gloucester, Massachusetts and in coastal towns in throughout Maine.

10.0 SUMMARY

This paper has described two possible inventions in the field of wastewater treatment technology. These inventions of 1) chemically enhanced primary wastewater treatment, and, 2) the use of chitosan in chemically enhanced wastewater treatment, are relevant at a time when a significant percent of wastewater treatment plants in the United States have yet to comply with the secondary treatment requirements of the 1972 Clean Water Act. These inventions seek to maximize the efficiency of the first stage in the treatment process through the use of small dosages of chemicals (metal salts or chitosan and a polyelectrolytic anionic polymer) and are able to operate at high efficiencies, both in terms of the removal of pollutants and in terms of overflow rates. Any follow-on treatment stage can be reduced in size by approximately 50%. In the event that an additional treatment stage is needed, the invention recommends the use of aerated biofilters over the conventional activated sludge process, as filters work well with low influent BOD and are thus the optimal concomitant of chemically enhanced primary treatment.

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APPENDIX A -- Congressional Testimony, S. Murcott, March, 1991.

APPENDIX B -- The Case for Chemically Enhanced Primary Treatment in a New Boston Harbor Cleanup Plan, Civil Engineering Practice, Spring, 1991

APPENDIX C -- MIT Sea Grant Article, May, 1991.

APPENDIX D -- United States Patents in the Field of Wastewater Treatment Technology

APPENDIX D
UNITED STATES PATENTS
IN THE FIELD OF WASTEWATER TREATMENT TECHNOLOGY

In order to determine whether the processes described in this paper are in fact patentable inventions, the author has researched the patent literature. This effort has had two effects:

- 1) It has provided a wider view of inventions in the field of wastewater treatment generally, and,
- 2) It has given a sharper focus to the specific invention described here.

This appendix summarizes some of the important discoveries in the field of wastewater treatment technology as described in United States patents issued from 1967 to the present. It is not intended as an exhaustive list, but hopefully is representative of significant advances that have taken place over the last 24 years.

1. U.S. Patent 3,337,454: Production of Potable Water From Effluent Sewage and Polluted Waters, Andrew Gruenwald, Hollis, N.Y. August 22, 1967.

This invention converts polluted or sewage water into potable, sanitary, and industrial purpose water. The process involves injecting a dispersion of powdered activated carbon and a solution of alum, causing settling and sedimentation (taking place over a period of 4 to 8 hours), decanting the water after settling and sedimentation, passing the water through a bed of highly chlorinated sand, and then passing the water under pressure through a bed of caustic treated granular activated carbon (using 5% aqueous caustic soda), then chlorinating and reaerating to obtain a potable water suitable for human consumption.

2. U.S. Patent 4,146,472: Process and Apparatus for Separating Matter in Suspension in a Liquid, Georges Treyssac, Marcq en Baroeul, France. March 27, 1979.

This invention is a flotation apparatus consisting of a treatment chamber. At one of its ends, it has an inlet for liquid to be treated, circulating without turbulence. At the other end it has an outlet for the treated liquid. There is a second inlet for water under high compression and charged with gas. This is located near to but below the first inlet. Then there is an outlet pipe for this high compression, gas-charged liquid, also near to and below the first outlet. This arrangement allows for the passage of micro-bubbles coming from the water under high compression to flow in a direction substantially parallel to the

direction of movement of the liquid to be treated. The intent is to create between the two ends of the chamber two distinct, superimposed and parallel flows, the upper one for the liquid to be treated, the lower one for the water under high compression.

3. U.S. Patent 4,371,440: Method of Treating a Wastewater Rich in Protein. Kiyoshi Yoshizawa, Tokyo, Japan. Feb. 1, 1983.

This is an invention of newly isolated yeast fungi which are capable of assimilating a high amount of protein when added to a wastewater rich in protein. The result is that the BOD of the wastewater is efficiently decreased.

4. U.S. Patent 4,765,900: Process for the Treatment of Waste, William Schwoyer, Boulder, Colorado. Aug. 23, 1988.

This invention is a method of treating organic waste by separating the liquid portion from the solid portion and reacting the solid portion in an accelerated wet oxidation reaction. This method includes using an internally-derived ash from the wet oxidation reaction to weight the organic waste, thereby increasing the rate at which the liquid phase can be separated from the solid phase. By first removing the liquid portion of the waste, the oxygen demand of the waste to be processed by wet oxidation is substantially lowered. Ammonia is removed from the liquid portion of the waste in a de-ammoniating step which is followed by biological decomposition to form a liquid stream. In one embodiment, the method includes further treatment of the liquid stream to substantially remove salts and using the resulting deionized stream to dilute the solid portion of the waste prior to wet oxidation.

5. U.S. Patent 4,765,908: Process and Composition for Removing Contaminants From Wastewater, Barbara Monick, Alexander Blake, Smithtown, N.Y. Aug. 23, 1988.

This invention is a method of removing a variety of contaminants from a wastewater system and producing a non-leachable sludge. The treatment method uses an alkali or alkaline carbonate; activated montmorillonite; a catalyst such as zirconium and polyelectrolyte; one or more flocculents such as a metal salt and calcium oxide, lime or calcium hydroxide; and bentonite. The chemicals are introduced and mixed with the wastewater, which is then filtered to produce a non-leachable sludge comprised of contaminants which were in the wastewater.

6. U.S. Patent 4,882,069: Method for the Treatment of Sewage and Other Impure Water, Anton Pohoreski, Saskatoon, Canada. Nov. 21, 1989

This invention involves adding to sewage or other impure water in a mixing zone three chemicals, no more than two of which

have been pre-mixed. These chemicals are: a) an inorganic coagulant; b) an anionic polymer c) a cationic polymer, with intimate mixing of the added chemicals with the sewage water. The process also includes the proviso that the inorganic coagulant, either alone or with the anionic or cationic polymer cannot be added last; and the anionic and cationic polymer cannot be intimately mixed and added together. This process provides chemically-treated effluent having large, compact, firmly bonded, substantially shear resistant and rapidly separable flocs. The flocs are separated from the liquid in a separating zone. Finally, the treated effluent is removed from the separating zone.

7. U.S. Patent 4,882,070: Waste Water Clarification, Harry Wardell, New Port Richey, Florida. Nov. 21, 1989.

A process for increasing the efficiency of a primary clarifier in raw wastewater clarification by reducing BOD and TSS by the sequential addition of: 1) a salt of a water soluble bi- or tri-valent metal and compositions or mixtures thereof, 2) fly-ash, and 3) a cationic surface active polymer which is comprised of a branched, high cationic charge density polyether amine solution at the primary clarifier and recovering the clarified effluent from the primary clarifier.

[Note: The key to this patent is the polyester amine polymer. This polymer is being used successfully at the chemical secondary treatment plant in Tacoma Washington, a plant mentioned in Table 1. The MIT group has met with H. Wardell on several occasions and tested his chemicals at the primary treatment plant in Salem, Massachusetts. Although our procedures are somewhat similar, we have not had significant success with the Wardell chemicals.]

8. U.S. Patent 4,975,197: Orbal Wastewater Treatment Process, John Wittman, New Berlin, Wisconsin. Dec. 4, 1990

The orbal wastewater treatment process includes a plurality of concentric annular basins or channels that have surface aeration, wastewater and recycled activated sludge. This is mixed into a first channel by means of the surface aeration and an oxygen-containing gas such as air. It then passes into the lower portion of the zone under conditions which produce a complete mix reaction and enough oxygen to meet the biological oxygen demands of the mixed liquor. The gas is introduced in the form of fine bubbles, having a diameter of less than 4 mm. The mixed liquor is sequentially oxidized in a second and third chamber by a combination of surface aeration and by introducing an oxygen-containing gas into the lower portions of the channels.